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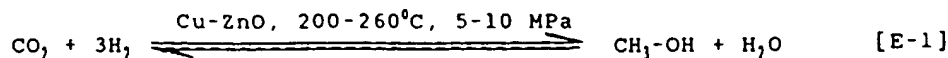
INTRODUCTION.

Our interest in the title originates from our efforts to develop an economically viable clean fuel process from natural gas. Natural gas, with its high calorific value (210.8 kcal/g-mol methane) is one of the most preferred fuels from the environmental point of view because of its clean burning characteristics. However, natural gas found in remote areas, far from markets, inaccessible to pipeline transportation, cannot be readily utilized. Currently several alternatives are practiced for remote natural gas utilization (1). Natural gas can be liquified by cooling to its boiling point (-163°C) and shipped in refrigerated containers. Natural gas can also be converted to methanol or hydrocarbon liquids (syncrude) or ammonia at its source, and these products shipped to market.

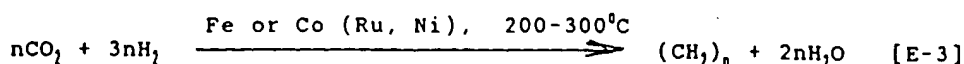
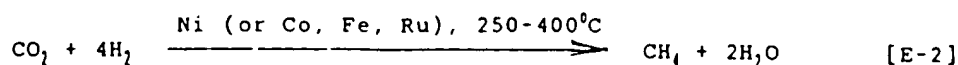
Both methanol and the Fischer-Tropsch (FT) hydrocarbon liquids are "clean fuels". Their fuel uses have been evaluated (2,3). Currently they cannot compete with the less expensive crude oil-derived fuels. Methanol commands a higher price as a "chemical", but this market is relatively small (estimated 27 MM tons per annum, worldwide) compared to the huge fuel market. Increasing percentage of the methanol production originates from remote gas using giant plants (800-975 M ton/annum capacity), taking advantage of the low gas costs and the economics of large scale production. Historically, the methanol market can be characterized by periods of shortages and periods of overproduction and low capacity utilization. Recently we proposed the development of a methanol-syncrude coproduction technology (4) which could keep the methanol plants running at full capacity even in case of methanol oversupply. The co-production scheme of Figure 1 would provide both economic and technological advances. In the first step, the compressed synthesis gas would be partially converted to methanol. This reaction has equilibrium limitations. The unconverted syngas from the methanol reactor would be converted to hydrocarbons. This latter reaction has no equilibrium limitations. We are currently working on the details of a research and development plan to demonstrate the viability of a co-production technology. The key to success depends on the demonstration that the effluents of the methanol reactor (a mixture of H₂, CO and CO₂) can be efficiently converted to high molecular weight FT products. The perceived difficulty is caused by the presence of carbon dioxide, which is known to yield preferentially methane rather than high molecular weight FT products in reductions (5). This study was undertaken to provide a stimulus for the development of a methanol-syncrude coproduction technology. Reported cases of carbon dioxide reductions to reasonably high molecular weight FT products already exist. The study should be helpful to set the stage for further progress.

HISTORICAL OVERVIEW OF CARBON DIOXIDE REDUCTIONS.

The reactions, utilization and sources of carbon dioxide have recently attracted considerable interest because of the possible ecological effects arising from large scale carbon dioxide emissions into the atmosphere. An information update is provided in very recent reviews by Xiaoding and Moulijn (6) on CO₂ reactions and usage; by Krylov and Mamedov (5) on its heterogeneous catalytic reactions; by Jessop, Ikariya and Noyori (7) on its homogeneous catalytic hydrogenations; by Tanaka on its fixation catalyzed by metal complexes (8); and by Edwards on its potential sources and utilizations (9). One of the most important reactions of carbon dioxide is its reduction to methanol:



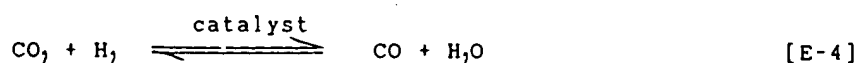
Although carbon dioxide has been reduced to methanol in the past in commercial operations (10,11), current methanol plants use mixtures of carbon dioxide and carbon monoxide. An alternative potential use of carbon dioxide would be its complete reduction to methane or to mixtures of Fischer-Tropsch type hydrocarbons:



Franz Fischer and coworkers were the first to try to reduce carbon dioxide to hydrocarbon oils, after their development of hydrocarbon synthesis from carbon monoxide. They have found, that carbon dioxide gives preferentially methane, with some gaseous homologues (12). However, liquid and solid hydrocarbons were also obtained in some experiments (13). These early reports have noted, that carbon monoxide was a reaction intermediate (12) and that liquid hydrocarbons were observed in those experiments, when the catalyst was alkalized or it contained a Cu component (13).

In the last decades, many chemists and surface scientists have extensively studied the reduction of carbon dioxide to hydrocarbons and the chemisorption of carbon dioxide on catalytic surfaces. It is out of the scope of this study to review the literature. However, a restricted number of references are cited (14-35) to sample the diversity of worldwide interests. The citations exclude the literature on carbon dioxide reductions to hydrocarbons which proceed via methanol intermediate.

The cited studies unanimously agree with the early conclusions that carbon monoxide is an intermediate formed by the reverse Water Gas Shift (WGS) reaction:



The reduction of carbon monoxide proceeds by the methanation reaction or FT synthesis. Falconer and Zagli have proposed (34) that the preferential formation of methane over higher hydrocarbons is caused by the high $\text{H}_2:\text{CO}$ ratio on the catalyst surface. While the major product was methane in most of the studies, a few cases of liquid hydrocarbon formation were also reported. Table 1 compiles the best examples of higher hydrocarbon formations. In the Table, we have converted the reported hydrocarbon selectivity data to Anderson-Schulz-Flory (ASF) growth probability values (alphas) to provide a basis for easy comparison of the product molecular weight distributions. ASF alpha values in the 0.6-0.7 range have been achieved, mostly on potassium-promoted Fe catalysts. Kuester (13) has evaluated different variations of unsupported, alkalized Co and Fe catalysts. In their work, reported in 1936, the formation of solid hydrocarbons (waxes) was often observed. Unfortunately, the reported product analyses were qualitative in nature and we were unable to derive chain growth probability values for product characterization. However, the isolation of waxes suggests that the chain growth probability values must have been substantially higher than 0.70, and probably were the highest in Table 1. In the penultimate example of Table 1, the primary olefinic products were converted to aromatic hydrocarbons over the ZSM-5 component of the catalyst. The last example of Table 1 is a case of higher hydrocarbon formation over $\text{Rh/Nb}_2\text{O}_3$. This appears to be an interesting case, since Rh is not known for FT catalysis.

In order to understand better how CO_2 reduction can be channeled toward higher hydrocarbon formation, relevant fundamental knowledge on the WGS and FT reactions will be reviewed and discussed below.

THE REVERSE WATER GAS SHIFT REACTION STEP.

The reduction of carbon dioxide to carbon monoxide, known as the reverse WGS reaction [E-4], has been extensively studied (36-39) because of its industrial importance in synthesis gas reactions and hydrogen manufacture. The most efficient heterogeneous catalysts for the WGS reaction are the Cu-based

catalysts, particularly Cu-Zn systems, the iron oxide based catalysts and the alkalized, sulfided Co-Mo catalysts (39). Other metals, oxides also have some catalytic effect, but they have received much less attention. However, alkalization was found to increase substantially the WGS activity of many substances (39). The alkalized FT catalysts have been extensively studied (13,40-43). Their WGS activity has been long known, but most of the cited studies focussed on the effect of alkali promotion on the changes in the rate and the products of the FT reaction. The alkalized FT catalysts seem to be excellent candidates for the reduction of carbon dioxide to FT hydrocarbons as the examples of Table 1 also suggest. Surface scientists have found (44-45) that alkalization of FT catalysts changes the relative chemisorptions of CO and H₂ and that alkalization activates the surfaces for CO₂ chemisorption (24,46).

Carbon dioxide hydrogenation to carbon monoxide [E-4] is a reversible reaction and leads to equilibrium. The equilibrium is independent of the pressure, but is very much influenced by the temperature. In the temperature ranges useful for the FT reaction, the equilibrium is not favorable. Figure 2 illustrates the equilibrium CO₂ conversions as a function of the temperature for 1:1, 3:1 and 4:1 H₂:CO₂ gas compositions. Higher CO₂ conversion can be obtained if the H₂ reagent is used in stoichiometric excess. The equilibrium will be also favorably shifted if the CO is removed from the system. This happens during reductions to the hydrocarbon stage.

THE FISCHER-TROPSCH REACTION STEP.

The FT reaction (E-3) has been very extensively studied because of its commercial significance and because of its scientific complexity and diversity. This brief review will be restricted to certain aspects of FT chemistry which are relevant to our objectives.

In first approximation, the products of the FT synthesis are defined by a single parameter, the chain growth probability (α or α) according to the ASF equation:

$$C_n = (\ln^2 \alpha) n \alpha^n \quad (E-5)$$

where C_n is the carbon selectivity (mass fraction in the ideal case when the products are olefins) of the product with n carbon number and α is the chain growth probability. In practice, a multiplicity of α 's is produced, but an "averaged α " still reasonably defines the products unless the range of the α 's is very broad (47). Deviations from the AFS distribution have been widely reported. Some of the deviations are predictable and well defined (48); others, notably the C1 selectivities, are not well defined.

For the purpose of this treatment, it is proposed, that methanation (E-2) is an extreme case of the FT reaction (E-3) when the chain growth probability value is zero or very low. This understanding seems to be supported by the numerous reports that small amounts of ethane and propane are usually also observed during methanation. The methanation catalysts are very active hydrogenation catalysts, and they hydrogenolize the metal-Cl intermediates on the catalyst surface before they could grow. Furthermore, the methanation catalysts can also hydrogenolize the higher hydrocarbons already formed, which reactions also produce methane. Because of these reactions, the ASF equations may increasingly fail to define the product distributions as the chain growth probability value decreases.

Recently we have proposed for Co/SiO₂ catalysts (47), that the chain growth probability is a function of the catalyst, of the reagent and inert concentrations and of the temperature of the catalyst surface:

$$\alpha = f(C, S_1, \dots, S_i, T) \quad (E-6)$$

Even though the function f cannot be defined, it may be beneficial to review our qualitative knowledge about the factors which together should define α . In E-6, C is the catalyst factor which is composed of numerous elements. The catalytic metal is important. Co, Fe and Ru are known to be able to produce very high α values. There are reports in the literature (49-51)

suggesting that the dispersion of the metal can influence chain growth. Promoters incorporated into the catalysts can also influence chain growth. Alkali metal salts, particularly K salts, were found to greatly increase chain growth (13,40-43). In addition, alkalization had a tremendous influence on the reaction characteristics by changing the relative strengths of H_2 , CO and CO_2 chemisorptions. The hydrogenating character of the catalyst was reduced by alkalization, resulting in high olefin yields.

In E-6, S_1, \dots, S_i represent the concentrations of the reagents and inerts (including products). The question is how to define these concentrations in light of the knowledge, that in most FT reactions diffusion controls the rates (47). Due to complex diffusion effects, the concentrations of the components in the immediate vicinity of the catalyst surface might be quite different, than their concentrations in the bulk gas phase. To eliminate the need for considering diffusion effects, S_1, \dots, S_i concentrations represent the concentrations of components A to Z in the immediate vicinity of the catalyst surface. The values of S_1, \dots, S_i are related to their respective bulk gas phase concentrations and are dependent on the prevailing diffusional conditions. Of course, their values can be changed by changing the pressure of the system. Qualitative examples on the influence of component concentration, pressure, diffusion on the chain growth probability are available in the literature. Thus, increasing $H_2:CO$ ratio was shown to give lower alpha values (47). Dilution of the feed with inert gases was also shown to result in lower chain growth probability (47). Diffusional changes were also suggested for observed changes in rate and chain growth probability (52).

The influence of the reaction temperature (T) on the value of the chain growth probability has been long known. Recently we have shown, that over Co catalysts, the alpha value sharply decreases with increasing T (47). Over alkalized Fe catalysts, as reviewed by Dry (43), the effect of T appears to be much more gradual. With these catalysts, chain growth probability of about 0.7 can be obtained even over 300°C. In Table 1, we can see an example of 0.72 chain growth probability from CO_2 reduction at 400°C over a "heavily alkalized" Fe catalyst.

CATALYST AND PROCESS DESIGN REQUIREMENTS.

From the above review it is clear, that a combination of appropriate catalyst design and process design is required for obtaining high molecular weight FT products in CO_2 reductions. The catalyst must contain a WGS component and a FT component. The WGS component must provide fast rates for CO formation and accumulation. Furthermore, the surfaces must be modified for obtaining a proper balance in the chemisorptions of CO_2 , CO and H_2 . Concerning the process design, the process parameters (T, P, SV, feed composition) need to be optimized for the individual catalyst to provide the most favorable $H_2:CO$ ratios on the catalyst surface for high molecular weight FT products. Conceptually, diffusion control might also serve to regulate the $H_2:CO$ ratio. If gas phase diffusion controls the reagent concentrations on the catalyst surface, the surface is expected to be enriched in hydrogen, because of its high diffusivity arising from its small molecular size [52]. If diffusion through liquids were to control the reagent concentrations on the catalyst surface, the excessive hydrogen concentration on the catalyst surface may be avoided, due to differences in the solubilities of the reagents in hydrocarbon liquids [53]. We are optimistic that utilization of knowledge in catalyst and process design will lead to significant increases in the ASF growth probability values during CO_2 reductions.

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Table 1. Reported Examples of Carbon Dioxide Reductions to Higher FT Hydrocarbons.¹

Catalyst	T (°C)	P (kPa)	% CO ₂ conversion ^b	α value ^c	Reference
Fe-K/Al ₂ O ₃	400	2026	69.6; 66.9	0.72	14
Fe-K/Al ₂ O ₃	300	1013	57.7; 50.4	0.66	18
Fe-Mn-K	320	1013	33.8; 29.0	0.56	22
Fe-K	320	1013	34.7; 28.4	0.65	28
Fe-Cu-KCl/ TiO ₂ -Al ₂ O ₃	270	1520	10.0; 5.3	0.68	33
Co, Fe-Cu, K	150-250	101	?	see text	13
Fused Fe-ZSM-5	350	2100	38.1; 32.6	see text	27
Rh/Nb ₂ O ₅	350	101	11; 10	0.21	29

^aThe H₂/CO₂ feed ratios varied between 4:1 and 1:1.

^bThe first number gives the total conversion (CO + hydrocarbons); the second number the conversion to hydrocarbons.

^cOur best estimates of the chain growth probabilities from the reported data, unless provided in the publication.

Figure 1. Conceptual Methanol-Syncrude Coproduction Scheme.

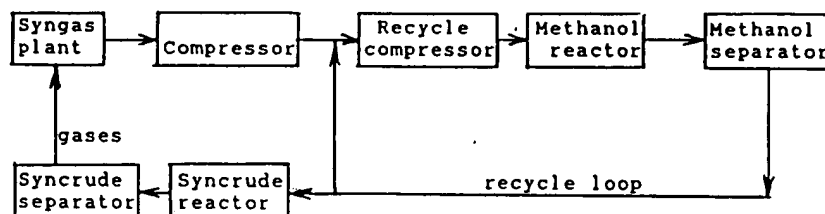


Figure 2. CARBON DIOXIDE CONVERSIONS IN REVERSE WGS EQUILIBRIA

